Friedelan-y-one (LXIXc) (R. M. Gascoigne), R. D. (Fig. 6) in dioxane (*c* 0.05): $[\alpha]_{700}$ −23°, $[\alpha]_{589}$ −15°, $[\alpha]_{322.5}$ −700°, $[\alpha]_{280}$ +664°, $[\alpha]_{275}$ +592°.

Methyl glycyrrhetate 3-acetate (LXX), R. D. (Fig. 7) in dioxane (*c* 0.1): $[\alpha]_{700}$ +70°, $[\alpha]_{589}$ +113°, $[\alpha]_{394}$ +294°, $[\alpha]_{380}$ +231°, $[\alpha]_{369-367.5}$ +309°, $[\alpha]_{362.5}$ +287°, $[\alpha]_{287.5}$ +1558°, $[\alpha]_{282.5}$ +1362°.

11-Keto-α-amyrin acetate (LXXI) (F. S. Spring), R. D. (Fig. 7) in dioxane (*c* 0.11): $[\alpha]_{700}$ +49°, $[\alpha]_{589}$ +91°, $[\alpha]_{410}$ +194° (sh.), $[\alpha]_{380}$ +36°, $[\alpha]_{369}$ +158°, $[\alpha]_{362.5}$ +91°, $[\alpha]_{350}$ +549°, $[\alpha]_{277.5}$ +2990°, $[\alpha]_{275}$ +2896°.

Δ^{12}-18α-Oleanen-3β-ol-11-one acetate (LXXII) (F. S. Spring), R. D. (Fig. 7) in dioxane (*c* 0.1): $[\alpha]_{700}$ +46°, $[\alpha]_{589}$ +65°, $[\alpha]_{450}$ +91° (sh.), $[\alpha]_{375}$ −522°, $[\alpha]_{365}$ −252°, $[\alpha]_{360}$ −371°, $[\alpha]_{310}$ +2157°, $[\alpha]_{300}$ +1827°.

Methyl 18α-glycyrrhetate (LXXIII) (F. S. Spring), R. D. in dioxane (*c* 0.1): $[\alpha]_{700}$ +62°, $[\alpha]_{589}$ +76°, $[\alpha]_{450}$ +111° (infl.), $[\alpha]_{440}$ +114° (sh.), $[\alpha]_{377.5}$ −341°, $[\alpha]_{367.5}$ −133°, $[\alpha]_{360}$ −204°, $[\alpha]_{317.5}$ +1836° (infl.), $[\alpha]_{317.5}$ +1836°, $[\alpha]_{275}$ +2964°.

11-Ketodumortierigenin (LXXIV), R. D. (Fig. 8) in dioxane (*c* 0.08): $[\alpha]_{700}$ −2°, $[\alpha]_{589}$ −17°, $[\alpha]_{425}$ −70°, $[\alpha]_{410}$ −58°, $[\alpha]_{382.5}$ −183°, $[\alpha]_{374}$ −138°, $[\alpha]_{367.5}$ −180°, $[\alpha]_{352.5}$ −46°, $[\alpha]_{350}$ −48°, $[\alpha]_{340}$ +101°, $[\alpha]_{337.5}$ +57°, $[\alpha]_{332.5}$ +83°, $[\alpha]_{331}$ +71°, $[\alpha]_{327.5}$ +100°, $[\alpha]_{297.5}$ −262°, $[\alpha]_{295}$ −258°, $[\alpha]_{292.5}$ −270°, $[\alpha]_{287.5}$ −232°, $[\alpha]_{285}$ −248°, $[\alpha]_{282.5}$ −238°.

$\Delta^{9(11)}$-Oleanen-3β-ol-12-one acetate (LXXV) (F. S. Spring), R. D. (Fig. 8) in dioxane (*c* 0.1): $[\alpha]_{700}$ +45°, $[\alpha]_{589}$ +62°, $[\alpha]_{380}$ +720°, $[\alpha]_{370}$ +598°, $[\alpha]_{365}$ +651°, $[\alpha]_{337.5}$ −284°, $[\alpha]_{336}$ −280°, $[\alpha]_{327.5}$ −424°, $[\alpha]_{277.5}$ +251°.

$\Delta^{9(11)}$-Oleanen-3β,28-diol-12-one diacetate (LXXVI),[77] R. D. in dioxane (*c* 0.25 (700–360 mμ), 0.055 (360–335 mμ)): $[\alpha]_{700}$ +39°, $[\alpha]_{589}$ +45°, $[\alpha]_{378}$ +656°, $[\alpha]_{365}$ +547°, $[\alpha]_{360}$ +568, $[\alpha]_{325}$ −325°, $[\alpha]_{285}$ +67°.

$\Delta^{9(11)}$-Ursen-3β-ol-12-one acetate (LXXVII) (F. S. Spring), R. D. in dioxane (*c* 0.09): $[\alpha]_{700}$ +52°, $[\alpha]_{589}$ +101°, $[\alpha]_{380}$ +1417°, $[\alpha]_{372.5}$ +1339°, $[\alpha]_{366}$ +1381°, $[\alpha]_{325}$ −1428°, $[\alpha]_{322.5}$ −1417°, $[\alpha]_{320}$ −1422°, $[\alpha]_{277.5}$ −560°.

$\Delta^{9(11)}$-18α-Oleanen-3β-ol-12-one acetate (LXXVIII) (F. S. Spring), R. D. (Fig. 8) in dioxane (*c* 0.09): $[\alpha]_{700}$ +96°, $[\alpha]_{589}$ +113°, $[\alpha]_{470}$ +154° (sh.), $[\alpha]_{370}$ −710°, $[\alpha]_{307.5}$ +3118° (sh.), $[\alpha]_{302.5}$ +3130° (infl.), $[\alpha]_{277.5}$ +3720°, $[\alpha]_{275}$ +3708°.

$\Delta^{9(11),14}$-Taraxeradien-3β-ol-12-one acetate (LXXIX), R. D. (Fig. 8) in dioxane (*c* 0.15): $[\alpha]_{700}$ −31°, $[\alpha]_{589}$ −46°, $[\alpha]_{550}$ −51° (infl.), $[\alpha]_{375}$ +1417°, $[\alpha]_{370-362.5}$ +1250° (sh.), $[\alpha]_{325}$ −3583°, $[\alpha]_{305}$ −2924°.

Iso-α-amyradien-3β-ol-12-one (LXXX) (O. Jeger), R. D. in dioxane (*c* 0.11): $[\alpha]_{700}$ −16°, $[\alpha]_{589}$ −13°, $[\alpha]_{362.5}$ +1989°, $[\alpha]_{305}$ −4641°, $[\alpha]_{285}$ −4562°.

$\Delta^{11,13(18)}$-Oleadien-3-one (LXXXI) (D. H. R. Barton), R. D. in dioxane (*c* 0.06): $[\alpha]_{700}$ −62°, $[\alpha]_{589}$ −82°, $[\alpha]_{400}$ −273°, $[\alpha]_{350}$ −527°, $[\alpha]_{320}$ −853°, $[\alpha]_{300}$ −1404°, $[\alpha]_{290}$ −2142°, $[\alpha]_{280}$ −3294°, $[\alpha]_{275}$ −3820°.

Methyl dehydro-oleanonate (LXXXII) (D. H. R. Barton), R. D. (Fig. 9) in dioxane (*c* 0.05): $[\alpha]_{700}$ −142°, $[\alpha]_{589}$ −176°, $[\alpha]_{400}$ −488°, $[\alpha]_{350}$ −892°, $[\alpha]_{320}$ −1478°, $[\alpha]_{300}$ −2364°, $[\alpha]_{290}$ −3416°, $[\alpha]_{280}$ −5296°, $[\alpha]_{275}$ −5992°.

Methyl isodehydro-oleanonate (LXXXIII) (D. H. R. Barton), R. D. (Fig. 9) in dioxane (*c* 0.03): $[\alpha]_{700}$ +77°, $[\alpha]_{589}$ +137°, $[\alpha]_{400}$ +540°, $[\alpha]_{350}$ +920°, $[\alpha]_{320}$ +1530°, $[\alpha]_{300}$ +2003°, $[\alpha]_{290}$ +2280°, $[\alpha]_{280}$ +2840°, $[\alpha]_{275}$ +3270°.

$\Delta^{9(11),12}$-Ursadien-3-one (LXXXIV) (D. H. R. Barton), R. D. (Fig. 9) in dioxane (*c* 0.1): $[\alpha]_{700}$ +238°, $[\alpha]_{589}$ +388°, $[\alpha]_{322.5}$ +6749°, $[\alpha]_{310}$ +4390.

Methyl dehydro-oleanolate acetate (background rotation for LXXXII) (D. H. R. Barton), R. D. in dioxane (*c* 0.15): $[\alpha]_{700}$ −80°, $[\alpha]_{589}$ −117°, $[\alpha]_{400}$ −512°, $[\alpha]_{350}$ −975°, $[\alpha]_{320}$ −1648°, $[\alpha]_{300}$ −2764°, $[\alpha]_{290}$ −3870°, $[\alpha]_{280}$ −5429°.

Methyl isodehydro-oleanolate (background rotation for LXXXIII) (D. H. R. Barton), R. D. in dioxane (*c* 0.098): $[\alpha]_{700}$ +134°, $[\alpha]_{589}$ +198°, $[\alpha]_{400}$ +641°, $[\alpha]_{350}$ +1088°, $[\alpha]_{320}$ +1609°, $[\alpha]_{300}$ +2321°, $[\alpha]_{290}$ +2913°, $[\alpha]_{280}$ +3660°.

$\Delta^{9(11),12}$-Ursadien-3β-ol (background rotation for LXXXIV) (D. H. R. Barton), R. D. in dioxane (*c* 0.10): $[\alpha]_{700}$ +234°, $[\alpha]_{589}$ +370°, $[\alpha]_{400}$ +1462°, $[\alpha]_{350}$ +3094°, $[\alpha]_{320}$ +7078°, $[\alpha]_{315}$ +7182°.

Zeorinone (D. H. R. Barton), R. D. in dioxane (*c* 0.105): $[\alpha]_{700}$ +10°, $[\alpha]_{589}$ +25°, $[\alpha]_{390-380}$ +58° (broad peak), $[\alpha]_{370-365}$ +36°) (sh.), $[\alpha]_{325}$ −164°, $[\alpha]_{287.5}$ +398°, $[\alpha]_{275}$ +347°.

DETROIT, MICH.

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[77] Unpublished work in this laboratory by Dr. G. Krakower.

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, THE WEIZMANN INSTITUTE OF SCIENCE]

Unsaturated Macrocyclic Compounds. VIII.[1] Oxidation of Terminal Diacetylenes to Large Ring Polyacetylenes with Cupric Acetate in Pyridine. Synthesis of Five New Macrocyclic Rings[2]

BY FRANZ SONDHEIMER, YAACOV AMIEL AND REUVEN WOLOVSKY

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The oxidative coupling of octa-1,7-diyne (IIa) with cupric acetate in pyridine has been shown to yield not only the cyclic dimer IIIa, but also the cyclic trimer Va, tetramer VIIa, pentamer IXa and higher cyclic polyacetylenes. Corresponding cyclic polyacetylenes have been obtained from nona-1,8-diyne (IIb), hepta-1,6-diyne (IIc) and deca-1,9-diyne (IId). Five new alicyclic ring systems (the 27-, 36-, 40-, 45- and 54-membered ones) have been prepared by this new method for constructing macrocyclic compounds, by which large rings can be prepared directly in one step from simple starting materials. Full hydrogenation of the cyclic polyacetylenes leads to the corresponding saturated hydrocarbons. The melting point behavior of the seven new cyclic paraffins thus obtained (the 20-, 21-, 27-, 36-, 40-, 45- and 54-membered ones) are briefly discussed.

The oxidative coupling of certain terminal diacetylenes of type II by means of oxygen in the presence of cuprous chloride and ammonium chloride in aqueous ethanol to yield cyclic "dimers" of type III besides linear products was described in parts III[3] and IV[4] of this series. We were beginning to study this type of coupling of terminal acetylenes in homogeneous media and also to investigate various reactions of the cyclic tetraacetylenes III when Eglinton and Galbraith[5] made the interesting announcement that oxidation of tetradeca-1,13-diyne (II, $n = 10$) with cupric acetate in methanol and pyridine under conditions of high dilution gives rise to a mixture of the cyclic monomer and the cyclic dimer (III, $n = 10$) in comparatively high yield.

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[1] For part VII, see F. Sondheimer, Y. Amiel and Y. Gaoni, THIS JOURNAL, **81**, 1771 (1959).

[2] Presented in part at the 16th International Congress of Pure and Applied Chemistry, Paris, July, 1957 (Congress Handbook, Division of Organic Chemistry, p. 156).

[3] F. Sondheimer and Y. Amiel, THIS JOURNAL, **79**, 5817 (1957).

[4] F. Sondheimer, Y. Amiel and R. Wolovsky, *ibid.*, **79**, 6263 (1957).

[5] G. Eglinton and A. R. Galbraith, *Chemistry & Industry*, 737 (1956).

In order to obtain an improved yield of our previously described cyclohexadeca-1,3,9,11-tetrayne (IIIa),[3] we employed the Eglinton–Galbraith type of conditions to oxidize octa-1,7-diyne (IIa). However for the sake of simplicity the reaction was not run under conditions of high dilution, 1 part of the diacetylene IIa simply being heated with 15 parts of neutral cupric acetate monohydrate in 100 parts of pyridine at 55° for 3 hours. The infrared spectrum of the total crystalline product showed it to be mainly cyclic in nature (bands at 4.45 and 4.64 μ due to disubstituted α-diacetylene, very weak band at 3.03 μ due to acetylenic hydrogen).[3,4] Crystallization yielded material which at first appeared simply to be the impure cyclic dimer IIIa. However the melting point was raised only gradually by repeated crystallization and it soon became apparent that in fact the product was a complex mixture. The best method of separation was found to be careful chromatography on at least 200 parts of alumina into over 200 fractions. This procedure showed that at least seven different cyclic substances had been formed, of which four could be identified.

The first substance to be eluted from the column, in 9% yield, showed m.p. 163° and had the empirical formula $(C_8H_8)_n$. It proved to be identical with the cyclic dimer cyclohexadeca-1,3,9,11-tetrayne (IIIa), obtained previously[3] in about the same yield. The second substance (m.p. 174°), obtained in 14% yield, differed from the cyclic dimer IIIa as evidenced by a depression in melting point on admixture. However the new compound was clearly closely related to IIIa, since the two substances had the same elemental composition[6] and similar infrared spectra (α-diacetylene group present, terminal acetylene absent). Full hydrogenation of the new compound yielded a saturated hydrocarbon, which was identified as the known cyclotetracosane (VIa)[7] by the melting point and molecular weight. The original substance is therefore the cyclic trimer, cyclotetracosa-1,3,9,11,17,19-hexayne (Va).[8]

The next substance in order of polarity was obtained in 8% yield and showed m.p. 155°. The melting point was depressed on admixture with the previously eluted compounds, despite the fact that the elemental analysis again indicated the formula $(C_8H_8)_n$ and the infrared data were rather similar to those of the previously described products. Full hydrogenation yielded a saturated hydrocarbon which must be the known cyclodotriacontane (VIIIa)[9] in view of its melting point and molecular weight. The substance from which it was derived is therefore the cyclic tetramer cyclodotriaconta-1,3,9,11,17,19,25,27-octayne (VIIa).

The last compound to be identified (9% yield) had m.p. 157°, depressed on admixture with the previously eluted substance. The empirical formula once more was $(C_8H_8)_n$ and the infrared spectrum showed it to be cyclic. Full hydrogenation yielded a saturated hydrocarbon, m.p. 77°, having the composition $(C_8H_{16})_n$ and a molecular weight showing it to be the new cyclotetracontane (Xa). The corresponding polyacetylene must therefore be the cyclic pentamer cyclotetraconta-1,3,9,11,17,19,25,27,33,35-decayne (IXa).

The final three substances in order of polarity obtained from the coupling of octa-1,7-diyne showed m.p. 189, 197 and 218°, respectively. The infrared spectra of these products were similar to those of the previous substances and clearly showed them to be cyclic. They are doubtlessly cyclic polyacetylenes of higher molecular weight and ring size than those described above, but they have not yet been identified.

The remarkable coupling of octa-1,7-diyne (IIa) to yield a variety of cyclic polyacetylenes of different ring size appears to be a comparatively general reaction and three other examples are given in this paper.

The coupling of the next higher homolog, nona-1,8-diyne (IIb), under the above described conditions again yielded a complex mixture consisting mainly of cyclic products. Eight separate compounds could be separated by chromatography on 200 parts of alumina into over 300 fractions.

The first substance (m.p. 212°) to be eluted from the column was obtained in 10% yield and was identical with the previously described cyclic dimer cycloöctadeca-1,3,10,12-tetrayne (IIIb).[4] The second, third and fourth substances showed m.p. 126, 136 and 145°, respectively and were obtained in a yield of 13, 11 and 4%. They were all cyclic since they showed no terminal acetylene band at *ca.* 3.03 μ in the infrared and the elemental analyses indicated the empirical formula $(C_9H_{10})_n$ for the second and the third substance (no satisfactory analysis could be obtained for the fourth). Full hydrogenation severally yielded the new cyclic paraffins cycloheptacosane (VIb), cyclohexatriacontane (VIIIb) and cyclopentatetracontane (Xb), as evidenced by the elemental analyses and by molecular weight determinations. The acetylenic substances are therefore the cyclic trimer (cycloheptacosa-1,3,10,12,19,21-hexayne) (Vb), tetramer (cyclohexatriaconta-1,3,10,12,19,21,28,30-octayne) (VIIb) and pentamer (cyclopentatetraconta-1,3,10,12,19,21,28,30,37,39-decayne) (IXb), respectively.

The fifth compound (m.p. 145°), obtained in 4% yield, was also cyclic (infrared) and had the empirical formula $(C_9H_{10})_n$. It is most probably the cyclic hexamer cyclotetrapentaconta-1,3,10,12,19,21,28,30,37,39,46,48-dodecayne (XIb), as it was eluted directly after the pentamer IXb and on full hydrogenation yielded a new cyclic paraffin which

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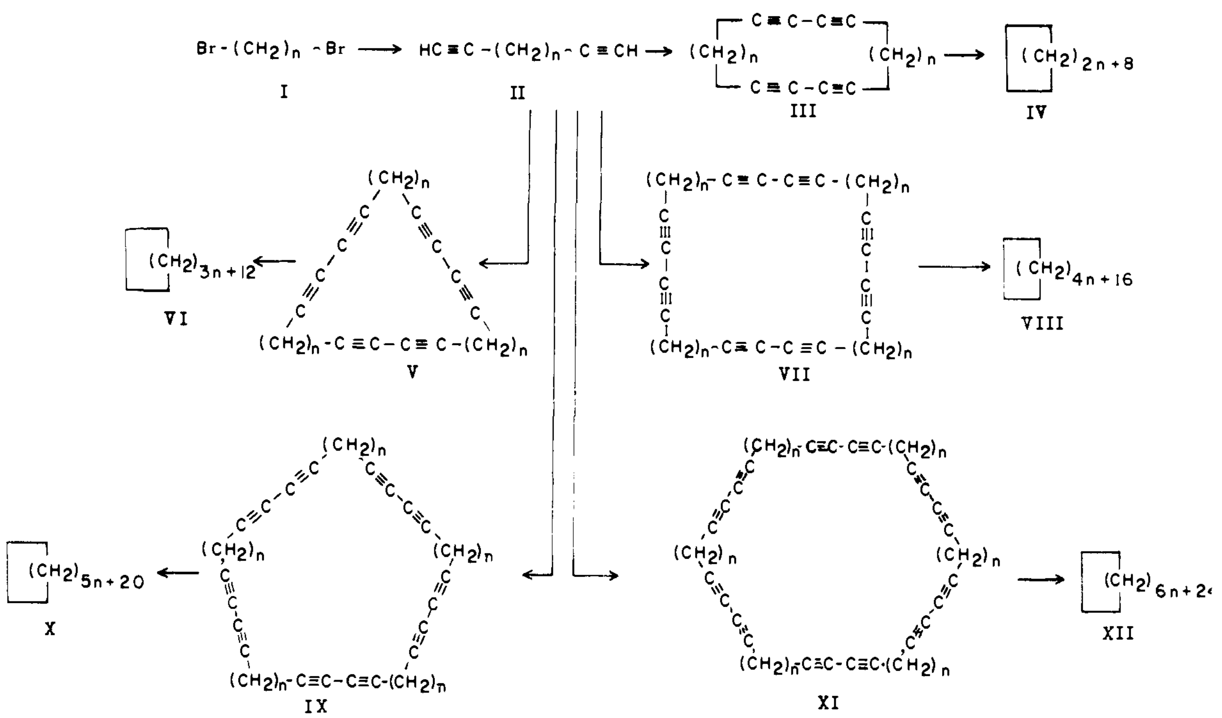
(6) In a preliminary communication (footnote 1), it was stated by us that most of the polyacetylenes exploded on attempted combustion and gave low carbon values. Since then Mr. E. Meier of our microanalytical laboratory has obtained satisfactory analytical results for practically all the polyacetylenes described in this paper, by carrying out the combustions slowly at a relatively low temperature, and by inserting a quartz plug behind the sample to prevent its dispersion on explosion.

(7) L. Ruzicka, M. Stoll, H. W. Huyser and H. A. Boekenoogen, *Helv. Chim. Acta*, **13**, 1152 (1930).

(8) After completion of most of the work reported in this paper, G. Eglinton and A. R. Galbraith (*Proc. Chem. Soc.*, 350 (1957)) described the preparation of the cyclic trimer of *o*-diethynylbenzene by the cupric acetate oxidation of the latter diacetylene. Added June 9, 1959.—Dr. Eglinton has informed us that this oxidation product is in fact the cyclic dimer (O. M. Behr, G. Eglinton and R. A. Raphael, *ibid.*, in press).

(9) L. Ruzicka, M. Hürbin and M. Furter, *Helv. Chim. Acta*, **17**, 78 (1934).



a, n = 4
b, n = 5
c, n = 3
d, n = 6

we believe to be cyclotetrapentacontane (XIIb). The formulation XIb for the polyacetylene could, however, not be proved conclusively since the saturated hydrocarbon was too insoluble for its molecular weight to be determined accurately and it is not impossible that it is a higher cyclic polymer.

The sixth and seventh compounds, showing m.p. 133 and 120° respectively, are undoubtedly cyclic products (infrared) of higher molecular weight and ring size than those described previously, but they have not yet been identified. Finally a substance with m.p. 94° was obtained which is linear, since it showed a strong terminal acetylene band at 3.02 μ in the infrared.

The coupling of hepta-1,6-diyne (IIc) with cupric acetate in pyridine again gave a complex mixture which was separated by chromatography as before. In this case only two cyclic products could be identified. The previously described rather unstable cyclic dimer IIIc[4] was not isolated; it may have been formed and destroyed under the reaction conditions employed. The first compound to be obtained (3% yield) showed m.p. 175°. It was cyclic (infrared) and showed the empirical formula $(C_7H_6)_n$. Full hydrogenation yielded the new cyclic paraffin cycloheneicosane (VIc) (elemental analysis, molecular weight determination) and the acetylenic compound is therefore the cyclic trimer cycloheneicosa-1,3,8,10,15,17-hexayne (Vc). The second product (m.p. 214°) was obtained in 4% yield and proved to be isomeric with the first. Full hydrogenation furnished the known cycloöctacosane (VIII)[7,9] and it is therefore the cyclic tetramercycloöctacosa-1,3,8,10,15,17,22,24-octayne (VIIc). Again cyclic products with higher molecular weight were formed but have not yet been investigated.

Finally the coupling of deca-1,9-diyne (IId) with cupric acetate and pyridine was studied. The resulting mixture on being resolved as before produced three separate cyclic substances which could be identified. These were obtained in yields of 3, 3 and 2% and showed m.p. 82, 136 and 154°, respectively. The infrared spectra showed the absence of terminal acetylene groups and the elemental analyses indicated the empirical formula $(C_{10}H_{12})_n$ for all three compounds. Full hydrogenation yielded, respectively, the hitherto unknown cycloeicosane (IVd) (elemental analysis and molecular weight determination), the known cyclotriacontane (VId)[7,9,10] and cyclotetracontane (VIIId); the last-mentioned hydrocarbon as expected was identical with Xa, the above-described full hydrogenation product of the cyclic pentamer IXa of octa-1,7-diyne. The three cyclic polyacetylenes are therefore the cyclic dimer (cycloeicosa-1,3,11,13-tetrayne (IIId), trimer (cyclotriaconta-1,3,11,13,21,23-hexayne) (Vd) and tetramer (cyclotetraconta-1,3,11,13,21,23,31,33-octayne) (VIId), respectively. Again higher cyclic polyacetylenes were obtained which have not been studied further. In addition a substance was eluted between the cyclic dimer IIId and trimer Vd which showed a strong terminal acetylene band at 3.03 μ in the infrared. This material is therefore linear and was not investigated.

The infrared spectra of the various cyclic polyacetylenes described in this paper are given in Table I. Measurements were made on potassium bromide pellets, since the spectra under these conditions were found to be better resolved compared with those taken previously in chloroform solu-

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(10) L. Ruzicka, W. Brugger, C. F. Seidel and H. Schinz, *Helv. Chim. Acta*, **11**, 496 (1928).

TABLE I

INFRARED SPECTRA OF CYCLIC POLYACETYLENES IN KBr[a]

IIIa	3.42s	4.45m	4.63m	6.90m	7.00s	7.35m	....	7.60s	7.81w	8.10w	....	8.49w	....	....	9.64s	.....	11.18m	.....	12.60w	13.53s	.....
IIIb	3.42s	4.45w	4.64m	6.86m	7.01s	7.31w	7.46s	7.58s	....	....	8.21m	....	....	9.25w	9.78w	.....	.....	12.20w	.....	13.56s	.....
IIIc[b]	3.42s	4.45m	4.64m	....	7.02s	....	....	7.61s	7.97s	....	....	....	8.60w	....	9.66s	.....	11.37s	12.03m	.....	.....	.....
IIId	3.42s	4.45w	4.63w	6.90s	7.00s	....	7.41s	7.59s	7.80m	8.05w	8.21w	....	8.71w	9.24m	....	10.22w	.....	11.96w	12.59w	.....	13.96m
Va	3.42s	4.46m	4.64m	6.88m	7.03s	7.33m	....	7.59s	7.88m	8.13w	....	8.49w	8.69w	9.42w	9.75m	.....	11.59w	12.29w	12.98m	13.59m	.....
Vb	3.42s	4.45w	4.64m	6.89m	7.02s	7.31m	7.46s	7.52s	7.79m	8.12w	8.20w	....	....	9.24w	9.79w	10.23w	11.51w	12.33w	.....	13.50m	13.95m
Vc	3.42s	4.45m	4.64m	6.90m	7.01s	....	....	7.56s	7.62s	8.07w	....	8.46w	....	....	9.67m	10.21w	11.18w	.....	.....	13.28m	.....
Vd	3.42s	4.45w	4.64w	6.83s	7.00s	7.36m	....	7.57s	7.87w	....	8.17w	8.46w	....	9.34w	9.59w	.....	.....	.....	....	.....	13.76m
VIIa	3.42s	4.45w	4.64m	6.88m	7.01s	7.32m	....	7.58s	7.87m	8.12w	....	8.41w	8.64w	9.40w	9.67w	.....	.....	.....	12.99m	13.61m	.....
VIIb	3.42s	4.45w	4.65w	6.83s	7.01s	7.32m	7.44s	7.55s	7.95m	....	8.16w	....	....	9.23w	9.44w	.....	.....	.....	.....	13.43m	13.77m
VIIc	3.42s	4.45w	4.63m	6.90m	7.01s	....	7.49s	7.60s	7.93w	8.11w	....	8.54w	....	9.48m	9.81w	10.17w	11.27w	.....	13.08m	.....	.....
VIId	3.41s	4.45w	4.65w	6.81s	7.00s	7.33w	....	7.56m	7.80w	8.08w	....	....	....	9.30w	9.60w	.....	.....	.....	13.02m	.....	13.83m
IXa	3.43s	4.45w	4.64m	6.88m	7.02s	7.33m	7.43m	7.56s	7.86w	8.09w	8.20w	8.46w	....	....	9.68m	.....	.....	.....	13.02m	.....	13.72m
IXb	3.42s	4.46w	4.65w	6.83s	7.00s	....	7.42m	7.55m	7.88w	....	....	....	....	....	9.73w	.....	.....	.....	.....	13.47m	13.84m
XIb	3.42s	4.45w	4.64w	6.82s	7.00s	....	7.45m	7.56s	7.66m	....	8.17w	8.41w	....	9.24w	9.68w	10.24w	.....	.....	.....	13.53m	13.82m

[a] λ_{max} in μ; s = strong; m = medium; w = weak.

tion.[3,4] As expected, a general family resemblance can be recognized, although of course individual differences above 7.5 μ exist.[11] In particular, all the substances show a doublet at *ca.* 4.45 and 4.65 μ due to the disubstituted α-diacetylene grouping. The strong band at *ca.* 3.03 μ (acetylenic C–H stretching) as well as the medium band at *ca.* 4.75 μ ($C\equiv CH$ stretching), shown by the starting materials II, were universally absent and this fact alone indicates all the compounds to be cyclic in nature.

The ultraviolet spectra of the cyclic polyacetylenes are given in the Experimental section. All the substances show the expected three maxima at *ca.* 227, 240 and 254 mμ due to the α-diacetylene group.[12] Intensities are recorded in only a few cases since generally the cyclic polyacetylenes were too insoluble in the isoöctane in which the measurements were made for accurate values to be obtained. It is of interest to recall that the cyclic dimer IIIc derived from hepta-1,6-diyne showed an anomalous ultraviolet spectrum[4] and this was interpreted as being due to the proximity of the two α-diacetylene groupings in IIIc. No such proximity effect would be anticipated in the corresponding cyclic trimer Vc and tetramer VIIc described in this paper and as expected the ultraviolet spectra of these substances are normal. Doubtlessly for the same reason the trimer Vc and tetramer VIIc exhibit normal melting points above 170°, whereas the dimer IIIc decomposed at *ca.* 115° on being heated.

All the cyclic polyacetylenes are highly crystalline colorless substances, which gradually form yellow or brown insoluble polymers on being allowed to stand at room temperature in air and light. They were stored most conveniently in benzene solution in the dark, and could then be kept almost indefinitely. Only a very few of the cyclic compounds formed bright colors on being allowed to stand in light, a phenomenon which is quite common with the linear dimers and tetramers.[4]

Various methods for determining the molecular weights of the cyclic polyacetylenes were tried unsuccessfully. Finally it was found that the molecular weights of the corresponding saturated cyclic paraffins could be determined accurately by the Rast method in camphene (instead of in the more usual camphor). The data thus obtained provided valuable information regarding the structures of the polyacetylenes.

The terminal acetylenes IIa–IId are easily made in quantity by the reaction of the dibromides Ia-Id with sodium acetylide in liquid ammonia.[13] The presently described work therefore provides a simple one-step method for preparing highly unsaturated large ring compounds over a wide range of size from readily available starting materials. In this paper macrocyclic polyacetylenes containing 16-, 18-, 20-, 21-, 24-, 27-, 28-, 30-, 32-, 36-, 40-, 45-

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(11) The infrared spectra of the polyacetylenes were not run at the same concentrations, so that no significance can be attached to the fact that some weak bands are shown by some substances and not by others.

(12) *Cf.* J. B. Armitage, C. L. Cook, N. Entwistle, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, 1998 (1952).

(13) (a) H. Bader, L. C. Cross, I. M. Heilbron and E. R. H. Jones, *ibid.*, 619 (1949); (b) A. L. Henne and K. W. Greenlee, THIS JOURNAL, **67**, 484 (1945); (c) W. M. Lauer and W. J. Gensler, *ibid.*, **67**, 1171 (1945).

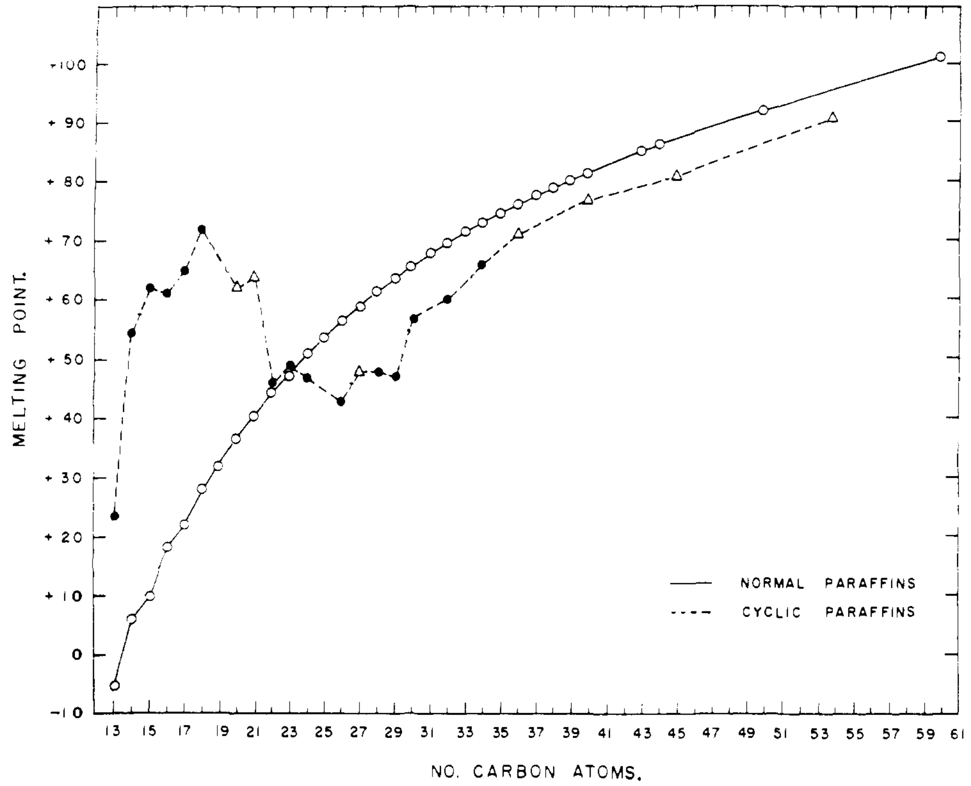

Fig. 1.—Melting point behavior of normal and cyclic paraffins.

and 54-membered rings have been synthesized. Of these, the 27-, 36-, 40-, 45- and 54-carbon compounds represent new ring systems. It is of interest that the largest monocyclic carbon ring prepared previously is 34-membered and the method presented in this paper makes available considerably larger rings than this, if desired.

Of the saturated cyclic paraffins prepared above, the ones containing 20, 21, 27, 36, 40, 45 and 54 carbon atoms in the ring are new. It has previously been pointed out[7,9,14] that if the melting point values of the cyclic paraffins from the 13-membered one onward[15] are plotted against ring size, a maximum occurs with the 18-membered ring. A minimum is then observed from the next higher known hydrocarbon, the 22-ring as far as the 29-ring. The melting point rises again, although only three further points (for the 30-, 32- and 34-rings) could be plotted. On the other hand, the melting points of the linear normal paraffins increase steadily with increasing molecular weight, the increase becoming quite regular from about *n*-octadecane onward.[15] The melting point curves of both the linear and cyclic paraffins are reproduced in Fig. 1 and the values for the seven new cyclic paraffins have been included (the new points are shown as Δ). It can be seen that the melting points of the 20- and 21-membered hydrocarbons fall between those of the 18- and 22-rings. The maximum therefore occurs either at the 18- or the still unknown 19-membered cyclic paraffin, as is the case with the corresponding ketones.[7,9] The melting point of the 27-membered compound falls into the general minimum which occurs between the 22- and 29-rings. As the rings become very large, any differences from the corresponding linear hydrocarbons should become less marked. As expected, the melting points of the largest rings after the 30-membered one rise steadily with increasing molecular weight, as do the melting points of the corresponding linear paraffins, the values for the cyclic substances being a few degrees lower.

Experimental[16]

Oxidative Coupling of Octa-1,7-diyne (IIa) with Cupric Acetate in Pyridine.—Pyridine (500 cc.; commercial grade, previously distilled over sodium hydroxide) was added to 75 g. of finely ground neutral cupric acetate monohydrate. The mixture was allowed to cool to room temperature and 5 g. of octa-1,7-diyne (IIa)[13a] was added. The mixture was then heated to 55° and stirred vigorously at this temperature under a reflux condenser for 3 hr., moisture being excluded. It was then cooled, filtered and the solid was washed well with benzene. The combined filtrates were evaporated nearly to dryness under reduced pressure and benzene and water were added. The organic extract was separated, washed well with dilute hydrochloric acid and water, dried and evaporated. The crystalline residue (4.3 g.) was mainly cyclic (only weak band at 3.03 μ in the infrared). One crys-

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(14) L. Ruzicka and G. Giacomello, *Helv. Chim. Acta*, **20**, 548 (1937).

(15) For a discussion of the melting point behavior of smaller cyclic paraffins, see L. Ruzicka, P. A. Plattner and H. Wild, *ibid.*, **29**, 1611 (1946).

(16) Melting points were taken on a Fisher-Johns apparatus and are uncorrected. All chromatograms were done with Alcoa activated alumina, grade F-20 (Aluminum Co. of America, Pittsburgh, Pa.). Infrared spectra were measured with a Baird double-beam recording spectrophotometer with sodium chloride optics on potassium bromide pellets. Ultraviolet spectra were determined in isoöctane solution on a Unicam model S.P. 500 spectrophotometer. The molecular weight determinations were made by the Rast method in camphene. We are indebted to Mr. Erich Meier and staff for the last-mentioned determinations as well as for all the microanalyses.

tallization from petroleum ether–chloroform gave cyclic crystalline material with m.p. *ca.* 130–140°.

The total residue (4.3 g.), which was not completely soluble in petroleum ether, was dissolved in benzene (15 cc.) and poured onto a column of 850 g. of alumina. The column was washed successively with pentane, petroleum ether, various mixtures of petroleum ether–benzene and finally with benzene, 40-cc. fractions being collected.

Fractions 68–80, eluted with petroleum ether–benzene (3:1 to 3:2), consisted of the cyclic dimer cyclohexadeca-1,3,9,11-tetrayne (IIIa) (0.422 g., 8.6%), m.p. 157–162°. Crystallization from petroleum ether–chloroform gave the pure material with m.p. 162–163°. Identity with the previously described substance (m.p. 160–162°)[3] was established through non-depression in m.p. on admixture and through infrared comparison. Further structure proof was provided through full hydrogenation to cyclohexadecane (IVa) with m.p. and mixture m.p. 60–61°.[3]

Fractions 84–96, eluted with petroleum ether–benzene (3:2), consisted of the cyclic trimer cyclotetracosa-1,3,9,-11,17,19-hexayne (Va) (0.688 g., 14.0%), m.p. 170–173°. Crystallization from petroleum ether–chloroform gave the analytical sample with m.p. 173–174°; λ_{max} 226, 240 and 254 mμ. A m.p. depression was observed on admixture with the cyclic dimer IIIa.

Anal. Calcd. for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found: C, 91.97; H, 7.88.

Full hydrogenation of Va and crystallization of the product from ethanol–ethyl acetate yielded cyclotetracosane (VIa) with m.p. 46.5–47°, reported[7] m.p. 46–47°.

Anal. Calcd. for $C_{24}H_{48}$: mol. wt., 337. Found: mol. wt., 330.

Fractions 104–118, also eluted with petroleum ether–benzene (3:2), consisted of the cyclic tetramer cyclodotriaconta-1,3,9,11,17,19,25,27-octayne (VIIa) (0.410 g., 8.4%), m.p. 150–154°. Crystallization from petroleum ether–chloroform led to the pure substance with m.p. 154–155°; λ_{max} 227, 240 and 254 mμ. A m.p. depression was observed on admixture with the cyclic trimer Va.

Anal. Calcd. for $C_{32}H_{32}$: C, 92.26; H, 7.74. Found: C, 92.04; H, 8.09.

Full hydrogenation of VIIa and crystallization of the product from ethanol–ethyl acetate produced cyclodotriacontane (VIIIa), m.p. 58–59°, reported[9] m.p. 59–60°.

Anal. Calcd. for $C_{32}H_{64}$: mol. wt., 449. Found: mol. wt., 429.

Fractions 126–165, also eluted with petroleum ether–benzene (3:2), consisted of the cyclic pentamer cyclotetraconta-1,3,9,11,17,19,25,27,33,35-decayne (IXa) (0.425 g., 8.7%), m.p. 144–150°. Crystallization from chloroform yielded the analytical sample with m.p. 155–157°; λ_{max} 226–227, 240 and 254 mμ. The m.p. was depressed on admixture with the cyclic tetramer VIIa. The substance rapidly becomes pink on being allowed to stand in daylight.

Anal. Calcd. for $C_{40}H_{40}$: C, 92.26; H, 7.74. Found: C, 91.89; H, 7.89.

Full hydrogenation of IXa, followed by crystallization from ethyl acetate or from chloroform, yielded the new cyclotetracontane (Xa) with m.p. 76–77°.

Anal. Calcd. for $C_{40}H_{80}$: C, 85.63; H, 14.37; mol. wt., 561. Found: C, 85.45; H, 14.15; mol. wt., 568.

Fractions 176–193 (0.845 g.), eluted with petroleum ether–benzene (1:1) and with pure benzene, all consisted of crystalline material with m.p. above 170°. These combined fractions were rechromatographed on 200 g. of alumina. Petroleum ether–benzene (1:1) yielded successively three substances with m.p. 188–189°, 195–197° and m.p. 216–218°, all showing infrared bands at 4.45 and 4.64 μ (disubstituted α-diacetylene present) but not at *ca.* 3.03 or 4.75 μ (terminal acetylene absent).

Oxidative Coupling of Nona-1,8-diyne (IIb).—The coupling of 5 g. of nona-1,8-diyne (IIa)[13b] with 75 g. of neutral cupric acetate monohydrate and 500 cc. of dry pyridine was carried out as described above for octa-1,7-diyne. Isolation with benzene as before yielded 5.15 g. of crystalline product with only a weak band at 3.03 μ (terminal acetylene) in the infrared. This material was dissolved in 15 cc. of benzene and chromatographed on 1 kg. of alumina. The column was washed with various mixtures of petroleum ether–benzene and then with pure benzene, 40-cc. fractions being collected.

Fractions 17–37, eluted with petroleum ether–benzene (3:1), consisted of the cyclic dimer cycloöctadeca-1,3,10,12-tetrayne (IIIb) (0.505 g., 10.3%), m.p. 206–210°. Crystallization from chloroform gave the pure substance with m.p. 210–212°, undepressed on admixture with the previously described substance (m.p. 210–212°).[4] Full hydrogenation yielded cycloöctadecane (IVb) with m.p. 71.5–72°, undepressed on admixture with an authentic sample.[4]

Fractions 45–78, eluted with petroleum ether–benzene (3:1), consisted of the cyclic trimer cycloheptacosa-1,3,10,-12,19,21-hexayne (Vb) (0.645 g., 13.1%) with m.p. 120–125°. Crystallization from ether gave a pure sample with m.p. 125–126°; λ_{max} 226, 240 and 254 mμ.

Anal. Calcd. for $C_{27}H_{30}$: C, 91.47; H, 8.53. Found: C, 91.66; H, 8.71.

Full hydrogenation of Vb and crystallization of the product from methanol–ethanol gave the new cycloheptacosane (VIb) with m.p. 47–48°.

Anal. Calcd. for $C_{27}H_{54}$: C, 85.63; H, 14.37; mol. wt., 379. Found: C, 85.94; H, 14.13; mol. wt., 374.

Fractions 90–146, eluted with petroleum ether–benzene (3:1 to 2:1), consisted of the cyclic tetramer cyclohexatriaconta-1,3,10,12,19,21,28,30-octayne (VIIb) (0.535 g., 10.9%) with m.p. 128–134°. Crystallization from petroleum ether–chloroform gave the analytical sample with m.p. 135–136°; λ_{max} 226, 240 and 254 mμ. A m.p. depression was observed on admixture with the cyclic trimer Vb.

Anal. Calcd. for $C_{36}H_{40}$: C, 91.47; H, 8.53. Found: C, 91.17; H, 8.65.

Full hydrogenation of VIIb and crystallization from ethyl acetate gave the previously unknown cyclohexatriacontane (VIIIb) with m.p. 70–71°.

Anal. Calcd. for $C_{36}H_{72}$: C, 85.63; H, 14.37; mol. wt., 505. Found: C, 85.58; H, 14.25; mol. wt., 517.

Fractions 162–204, eluted with petroleum ether–benzene (2:1 to 3:2), consisted of the cyclic pentamer cyclopentatetraconta-1,3,10,12,19,21,28,30,37,39-decayne(IXb) (0.185 g., 3.8%) with m.p. 135–140°. Crystallization from chloroform gave the pure compound with m.p. 144–145°, which strongly depressed the m.p. of the cyclic tetramer VIIb. No satisfactory analysis could be obtained for this substance.

Full hydrogenation of IXb and crystallization of the product from ethyl acetate yielded the new cyclopentatetracontane (Xb) with m.p. 80–81°.

Anal. Calcd. for $C_{45}H_{90}$: C, 85.63; H, 14.37; mol. wt., 631. Found: C, 85.76; H, 14.45; mol. wt., 618.

Fractions 220–235, eluted with petroleum ether–benzene (3:2), consisted of what is most probably the cyclic hexamer cyclotetrapentaconta-1,3,10,12,19,21,28,30,37,39,46,48-dodecayne (XIb) (0.195 g., 4.0%) with m.p. 138–144°. Crystallization from chloroform gave the analytical sample with m.p. 144–145°; λ_{max} 227, 240 and 254 mμ. A m.p. depression of almost 20° was observed on admixture with the cyclic pentamer IXb.

Anal. Calcd. for $C_{54}H_{60}$: C, 91.47; H, 8.53. Found: C, 91.33; H, 8.78.

Full hydrogenation of XIb and crystallization from chloroform gave the new cyclotetrapentacontane (XIIb) with m.p. 90–91°. The molecular weight could not be determined due to its insolubility in camphene.

Anal. Calcd. for $C_{54}H_{108}$: C, 85.63; H, 14.37. Found: C, 85.72; H, 14.40.

Fractions 240–254, eluted with petroleum ether–benzene (3:2), on crystallization from petroleum ether–ether yielded 70 mg. of a substance as plates with m.p. 131–133°, depressing the m.p. of the cyclic hexamer XIb. Fractions 255–275, eluted with petroleum ether–benzene (1:1 to 1:2), yielded 65 mg. of another substance with m.p. 118–120°. The infrared spectra of both these compounds clearly showed them to be cyclic.

Fractions 281–286, eluted with benzene, consisted of a compound (0.31 g.) which after crystallization from petroleum ether–chloroform showed m.p. 91–94°, strong infrared band at 3.02 μ (free ethinyl group); the substance is therefore linear.

Oxidative Coupling of Hepta-1,6-diyne (IIc).—The coupling of 5 g. of hepta-1,6-diyne (IIc)[13b] with 75 g. of neutral cupric acetate monohydrate and 500 cc. of dry pyridine was carried out at 55° as described above, except that the heating time was only 1.5 hr. The mixture was cooled, filtered, and the solid was extracted in a Soxhlet apparatus with boiling benzene until no further material was extracted (this procedure was found necessary to obtain a good recovery of organic product). Isolation was then carried out as previously. The resulting total product (5.25 g.) was dissolved in 30 cc. of benzene and chromatographed on 1 kg. of alumina. The column was washed first with petroleum ether, then with various mixtures of petroleum ether–benzene and finally with benzene, 40-cc. fractions being collected.

Fractions 127–140, eluted with petroleum ether–benzene (2:3), consisted of the cyclic trimer cycloheneicosa-1,3,8,-10,15,17-hexayne (Vc) (0.145 g., 3.0%), m.p. 170–175°. Crystallization from ether yielded a pure sample with m.p. 174–175°; λ_{max} 228, 242 and 256 mμ (ϵ, 1120, 1160 and 840, respectively).

Anal. Calcd. for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found: C, 92.88; H, 6.91.

Full hydrogenation of Vc and crystallization of the product from methanol–ethyl acetate yielded the new cycloheneicosane (VIc) with m.p. 63–64°.

Anal. Calcd. for $C_{21}H_{42}$: C, 85.63; H, 14.37; mol. wt., 295. Found: C, 85.66; H, 14.30; mol. wt., 289.

Fractions 144–152, also eluted with petroleum ether–benzene (2:3), consisted of the cyclic tetramer cycloöctacosa-1,3,8,10,15,17,22,24-octayne (VIIc) (0.185 g., 3.8%), m.p. 206–212°. Crystallization from ether gave the analytical sample with m.p. 213–214°; λ_{max} 226, 241 and 255 μ.

Anal. Calcd. for $C_{28}H_{24}$: C, 93.29; H, 6.71. Found: C, 92.98; H, 6.90.

Full hydrogenation of VIIc followed by crystallization of the product from methanol–ethyl acetate gave cycloöctacosane (VIIIc) with m.p. 47–48°, reported[7,9] m.p. 47–48°.

Anal. Calcd. for $C_{28}H_{56}$: mol. wt., 393. Found: mol. wt., 389.

Fractions 160–240, eluted with petroleum ether–benzene (2:3 to 1:3), consisted of an oil (0.51 g.) which crystallized in part. Fractions 246–265, eluted with benzene, on crystallization from ether yielded 0.055 g. of a substance with m.p. 97–98°, which rapidly became blue in light. The infrared spectra of both these materials (bands at 4.46 and 4.64 μ, no bands at 3.03 or 4.75 μ) showed them to be cyclic, but they have not been investigated further.

Oxidative Coupling of Deca-1,9-diyne (IId).—The coupling of 5 g. of deca-1,9-diyne (IId)[13c] with 75 g. of neutral cupric acetate monohydrate and 500 cc. of dry pyridine was performed as described above for octa-1,7-diyne (IIa). The total product (5.2 g.) showed only a weak band at 3.02 μ (terminal acetylene) in the infrared. It was dissolved in 30 cc. of benzene and chromatographed on 1 kg. of alumina. The column was washed successively with petroleum ether, various mixtures of petroleum ether–ether and finally with pure ether, 100-cc. fractions being collected.

Fractions 44–57, eluted with petroleum ether–ether (92.5:-7.5), consisted of the cyclic dimer cycloeicosa-1,3,11,13-tetrayne (IIId) (0.142 g., 2.9%), m.p. 78–80°. Crystallization from petroleum ether yielded the analytical sample as needles with m.p. 81–82°; λ_{max} 226, 240 and 254 mμ (ϵ, 870, 850 and 520, respectively).

Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.57; H, 8.82.

Full hydrogenation of IIId and subsequent crystallization from methanol–ethyl acetate yielded the new cycloeicosane (IVd) with m.p. 61–62°.

Anal. Calcd. for $C_{20}H_{40}$: C, 85.63; H, 14.37; mol. wt., 281. Found: C, 85.73; H, 14.05; mol. wt., 270.

Fractions 81–99, eluted with petroleum ether–ether (85:15), contained a linear compound (strong band at 3.03 μ in the infrared) and were not investigated further.

Fractions 119–139, eluted with petroleum ether–ether (80:20), consisted of the cyclic trimer cyclotriaconta-1,3,-11,13,21,23-hexayne (Vd) (0.166 g., 3.4%), m.p. 128–134°. Crystallization from petroleum ether gave a pure sample as needles with m.p. 135–136°; λ_{max} 226, 240 and 254 mμ (ϵ 1030, 1030 and 620, respectively).

Anal. Calcd. for $C_{30}H_{36}$: C, 90.85; H, 9.15. Found: C, 90.50; H, 9.37.

Full hydrogenation of Vd and crystallization from methanol–ethyl acetate furnished cyclotriacontane (VId) with m.p. 57–58°, strongly depressed on admixture with the above-described cycloeicosane (IVd); reported[9] m.p. 57–58°.

Anal. Calcd. for $C_{30}H_{60}$: mol. wt., 421. Found: mol. wt., 416.

Fractions 166–186, eluted with petroleum ether–ether (70:30), consisted of the cyclic tetramer cyclotetraconta-1,3,11,13,21,23,31,33-octayne (VIId) (0.110 g., 2.2%), m.p. 146–150°. Crystallization from benzene–petroleum ether gave the analytical sample as plates with m.p. 152–154°; λ_{max} 226, 239 and 254 mμ. The m.p. was depressed on admixture with the cyclic trimer Vd.

Anal. Calcd. for $C_{40}H_{48}$: C, 90.85; H, 9.15. Found: C, 90.19; H, 8.93.

Full hydrogenation of VIId and crystallization from methanol–ethyl acetate yielded cyclotetracontane (VIIId) with m.p. 76.5–77°, undepressed on admixture with the sample obtained by the full hydrogenation of the cyclic pentamer IXa of octa-1,7-diyne (see above).

The last chromatographic fractions again contained crystalline higher cyclic polyacetylenes (no band at 3.03 μ in the infrared) which have not yet been investigated further.

Full Hydrogenations.—All full hydrogenations were carried out by shaking the cyclic polyacetylene (*ca.* 25 mg.), dissolved in 10 cc. of dioxane, in hydrogen over *ca.* 50 mg. of a prereduced platinum catalyst at room temperature and atmospheric pressure. When no more gas was absorbed, the catalyst was removed by filtration, washed well with hot dioxane, and the solvent was evaporated. The crystalline residue was dissolved in a little pentane (or benzene for the higher molecular weight hydrocarbons) and filtered through *ca.* 1 g. of alumina. The solvent was again evaporated and the residue crystallized from the specified solvent.

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[CONTRIBUTION FROM THE FRUIT AND VEGETABLE CHEMISTRY LABORATORY, A LABORATORY OF THE WESTERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION, AGRICULTURAL RESEARCH SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

Plant Polyphenols. VI. Experiments on the Synthesis of 3,3'- and 4,4'-Di-O-Methylellagic Acid[1]

BY LEONARD JURD

RECEIVED JANUARY 20, 1959

Improved procedures for the synthesis of monoalkyl-gallic acids, ellagic acid 4,4'-diacetate and the isomeric 3,3'- and 4,4'-di-O-methylellagic acids have been developed. 3,3'-Di-O-methylflavellagic acid and 3,3',4-tri-O-methyl- and tri-O-benzylellagic acids were isolated as side products in some of these reactions.

Alkylated gallic and ellagic acid derivatives have become increasingly important in studies on the naturally occurring gallotannins and ellagitannins. Many of the partial methyl ethers have been prepared; however, in some cases the reactions used have not given satisfactory yields of these ethers.

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